

13

Example 7

A Terpolymer of 15 Mole Percent DVS-bisBCB, 15 Mole Percent BCB Ethyl Acrylate and 70 Mole Percent BCB Acrylic Acid

DVS-bisBCB (9.59 g, 0.0246 mole), BCB ethyl acrylate (4.98 g, 0.0246 mole) and BCB acrylic acid (20 g, 0.115 mole) were heated in 105 g dipropyl glycol methyl ether acetate at 165° C. for 48 hours. The solution was cooled to room temperature. A film on the Si wafer was generated by spin-coating and curing at 250° C.

Example 8

Preparation of BCB-t-butyl Acrylate

A 5 liter three necked flask, equipped with a heating mantle, bottom dump valve, thermowell, reflux condenser and stirrer was charged with 1.43 grams of palladium acetate, 7.78 g of tris-(o-tolyl)-phosphine (TOTP), 356.8 g of 4-bromobenzocyclobutene (BrBCB), 250 grams of t-butyl acrylate, 385 g of potassium acetate, 585 mL of N,N-dimethylformamide (DMF) and 292 mL of deionized water. The reactor was degassed with a nitrogen sparge for 10 minutes and then heated to 93° C. After 19 hours a sample analyzed by capillary gas chromatography found no BrBCB and 91% trans-t-butyl acrylate BCB. After 22 hours the reactor was cooled and 1 liter of deionized water was added. The water layer was separated and discarded. The mixture was diluted with 1 liter of toluene and the organic phase washed with five 1-liter portions of deionized water. The organic phase was filtered through 150 mL of silica gel, topped with 40 g of magnesium sulfate on a membrane filter.

The toluene was removed by a rotary evaporator at aspirator vacuum using a 60° C. water bath, leaving 374.5 grams of crude product. The crude product was distilled at 120° C. and 0.005 torr. The overheads cut was 258.3 grams.

Example 9

Use of BCB-t-butyl Acrylate

BCB-t-butyl acrylate (34.5 grams), DVS-bisBCB (19.5 grams) and 162 grams of mesitylene were heated at 165° C. for over 66 hours. The solution was cooled to room temperature and filtered through a medium sintered glass filter. Part of the solution was spin-coated on a silicon wafer. The wafer was immersed in a TMAH solution. The spin-coated film started to break up in 10 seconds and dissolved in 50 seconds.

NMR spectra of DVS-bisBCB/t-butyl acrylate BCB prepolymers showed significant loss of the t-butyl group, ranging from 20% loss for a copolymer having 30 weight % t-butylacrylate BCB to 43% for a copolymer having 75 weight % t-butyl acrylate BCB. The presence of an acid group on the prepolymer was confirmed by IR spectroscopy. The IR spectra showed absorption at 1695 cm⁻¹ which is consistent with the presence of a carboxylic acid group.

Example 10

Use of DVS-bisBCB/BCB Acrylic Acid Copolymer in Wet Etching

DVS-bisBCB (17.60 grams, 0.0451 mol), BCB-acrylic acid (11.78 grams, 0.0677 mol) and mesitylene (28 grams) were heated with stirring under nitrogen at 165° C. for 69 hours. The solution was spread on a 4 inch wafer at 500 rpm followed by spin-coating at 3500 rpm. The wafer was baked on a hot plate at 100° C. for 2 minutes. A photoresist, Microposit 1400 from Shipley Company, was spread on top of the BCB film at 500 rpm for 1 second and spin-coated at 3000 rpm for 30 seconds. The wafer was baked in an oven at 100° C. for 15 minutes followed by exposure at 150 mJ/cm². The wafer was placed in a 2.3% Me₄NOH bath for

14

10 minutes to remove photoresist and BCB film in exposed areas. Water was used to rinse the etched wafer. The etched wafer was dried and flood exposed at 200 mJ/cm². Photoresist was removed by putting the wafer in an Me₄NOH solution for 2 minutes. The wafer with a patterned BCB film was rinsed with water and cured.

Example 11

Use of DVS-bisBCB/BCB Acrylic Acid (mole ratio 30:70) in an Aqueous Base Developable Negative Tone Photoimaging System

DVS-bisBCB (28.0 grams, 0.072 mole), BCB acrylic acid (29.1 grams, 0.167 mole) and 172 grams mesitylene were heated at 160° C. for 174 hours. DVS-bisBCB to BCB acrylic acid was 30/70 and percentage of solids was 25. Some solvent escaped during B-staging and the solution concentration was 39% with viscosity at 128 Centipoise. Some mesitylene was removed to generate a solution with 49% solids.

The B-staged solution (1.76 grams, 0.862 g prepolymer) and 1,6-bis(4-azidobenzylidene)-4-ethylcyclohexanone (41.7 mg, 4.6%) were mixed. Cyclohexanone (0.12 grams) was added to generate a homogeneous solution. The solution was spin-coated on a 4 inch wafer at 1500 rpm. Prebake time at 95° C. was 110 seconds. The wafer was exposed at 300 mJ/cm² with a mask. Development was performed in a 1.4% TMAH solution for 2 minutes and 13 seconds. The wafer was baked at 75° C. for 1.5 hours and then cured. Patterned film thickness was 2.5 microns.

What is claimed is:

1. A curable polymer comprising the partially polymerized product of at least one cyclobutane monomer wherein the product comprises a pendant group comprising a —COOH moiety in amounts defined by equivalent weights in the range of about 200 to about 330 g/mole of —COOH moiety.

2. The polymer of claim 1 wherein the equivalent weight is in the range of about 220 to about 300 g/mole of acid functionality.

3. The polymer of claim 1 wherein the equivalent weight is in the range of about 230 to about 270 g/mole of acid functionality.

4. The polymer of claim 1 wherein the polymerization occurs in a solvent selected from di(propylene glycol) methyl ether acetate isomers; toluene; xylene; mesitylene; alcohols having from 3 to 6 carbon atoms; methylcyclohexanone; N-methylpyrrolidone; butyrolactone; and dipropylene glycol dimethyl ether isomers.

5. The polymer of claim 1 having a molecular weight in the range of 1000 to about 50,000 grams/mol.

6. The polymer of claim 1 having a molecular weight in the range of 1500 to 25,000 grams/mol.

7. The polymer of claim 1 having a molecular weight in the range of 2000 to 15,000 grams/mol.

8. A photoreactive polymeric composition comprising the polymer of claim 1 and a photoactive composition such that the polymeric composition is rendered either soluble or insoluble upon exposure to activating wavelengths of radiation.

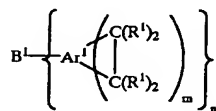
9. The polymeric composition of claim 8 wherein the photoactive composition comprises a dissolution inhibitor such that the polymeric composition is rendered soluble upon exposure to activating radiation.

10. The composition of claim 9 wherein the photoactive composition comprises a compound selected from sulfonylesters of trihydroxybenzophenone and cumyl phenol.

11. The composition of claim 8 wherein the photoactive composition comprises a photo-initiator that initiates further cure of the polymer upon exposure to activating radiation.

15

12. The composition of claim 8 wherein the polymer or oligomer is the partially polymerized product of monomers comprising (a) a cyclobutarene monomer having the formula:



wherein

B¹ is an n-valent organic linking group,

Ar^1 is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar^1 ;

m is an integer of 1 or more;

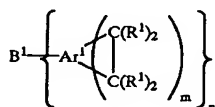
n is an integer of 1 or more; and

R^1 is a monovalent group; and

(b) is a cyclobutarene monomer comprising a —COOH moiety.

13. The polymer of claim 1, which is the partially polymerized product of monomers comprising:

(a) a cyclobutarene monomer having the formula:



wherein

B¹ is an n-valent organic linking group;

Ar¹ is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar¹:

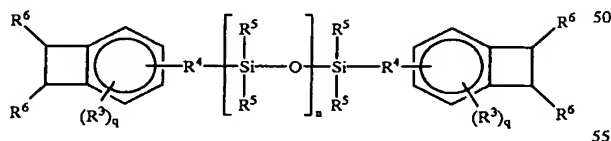
m is an integer of 1 or more;

n is an integer of 1 or more; and

R^1 is a monovalent group; and

(b) a cyclobutarene monomer comprising a $-\text{COOH}$ moiety.

14. The polymer of claim 13 wherein monomer (a) has the following formula:

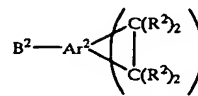


wherein each R³ is independently an alkyl group of 1-6 carbon atoms, trimethylsilyl, methoxy or chloro; each R⁴ is independently a divalent, ethylenically unsaturated organic group; each R⁵ is independently hydrogen, an alkyl group of 1 to 6 carbon atoms, cycloalkyl, aralkyl or phenyl; each R⁶ is independently hydrogen, an alkyl group of 1 to 6 carbon atoms, chloro or cyano; n is an integer of 1 or more; and each q is an integer of 0 to 3.

15. The polymer of claim 14 wherein R^4 is $-\text{CH}_2=\text{CH}_2-$, R^5 is methyl, R^6 is hydrogen, n is 1 and q is 0.

16

16. The polymer of claim 13 wherein the monomer (b) has the following formula:



wherein

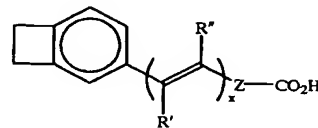
B² is a monovalent organic group comprising a —COOH moiety;

Ar^2 is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar^2 .

p is an integer of 1 or more; and

R^2 is a monovalent group.

17. The polymer of claim 13 wherein monomer (b) has the formula:



wherein

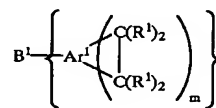
R' and R" are independently selected from hydrogen, alkyl groups of 1 to 6 carbon atoms, aryl groups, or R' and R" taken together from a cyclic group of 4 to 8 carbon atoms;

Z is a carbon-to-carbon bond or an aryl group; and

x is an integer from 0 to 3.

18. The polymer of claim 1, which is the partially polymerized product of monomers comprising:

(a) a cyclobutarene monomer having the formula:



wherein

B¹ is an n-valent organic linking group;

Ar¹ is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar¹;

m is an integer of 1 or more;

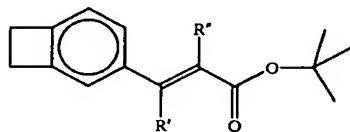
n is an integer of 1 or more; and

R^1 is a monovalent group; and

(b) is a cyclobutarene monomer having a pendant group, which at least partially converts to a carboxylic acid moiety during the polymerization process or by hydrolysis.

17

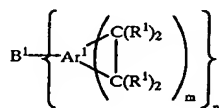
19. The polymer of claim 18 wherein (b') has the formula



wherein R' and R'' are independently selected from hydrogen, alkyl groups of 1 to 6 carbon atoms, aryl groups, or R' and R'' taken together from a cyclic group of 4 to 8 carbon atoms.

20. A process for making the polymer of claim 1 comprising the steps of

- (1) combining, in a solvent selected from di(propylene glycol) methyl ether acetate isomers; toluene; xylene; mesitylene; alcohols having from 3 to 6 carbon atoms; methylcyclohexanone; N-methylpyrrolidone; butyrolactone; and dipropylene glycol dimethyl ether isomers, a monomer (a) having the formula



wherein

B¹ is an n-valent organic linking group,

Ar¹ is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar¹;

m is an integer of 1 or more;

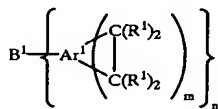
n is an integer of 1 or more;

with a monomer selected from monomer (b), which is a cyclobutene monomer comprising a carboxylic acid moiety and the monomer (b'), which is a cyclobutene monomer having a pendant group, which at least partially converts to a carboxylic acid moiety during the polymerization process; and

- (2) heating the combination to react with the monomers.

21. A partially polymerized product of monomers comprising

a cyclobutene monomer (a) having the formula:



wherein

B¹ is an n-valent organic linking group;

Ar¹ is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar¹;

m is an integer of 1 or more;

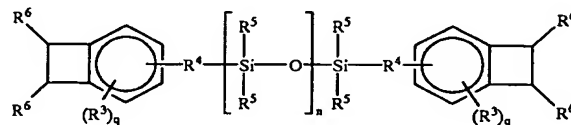
n is an integer of 1 or more; and

R¹ is a monovalent group; and

18

(b') is a cyclobutene monomer having a pendant group, which at least partially converts to a carboxylic acid during the polymerization process.

22. A curable polymer comprising the partially polymerized product of (a) a monomer of the formula:



wherein

each R³ is independently an alkyl group of 1-6 carbon atoms, trimethylsilyl, methoxy or chloro;

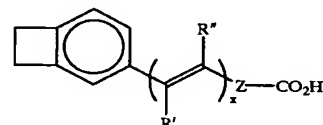
each R⁴ is independently a divalent, ethylenically unsaturated organic each R⁵ is independently hydrogen, an alkyl group of 1 to 6 carbon atoms, cycloalkyl, aralkyl or phenyl;

each R⁶ is independently hydrogen, an alkyl group of 1 to 6 carbon atoms, chloro or cyano;

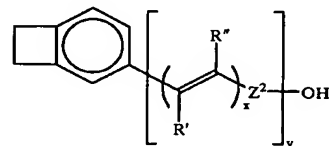
n is an integer of 1 or more; and

each q is an integer of 0 to 3; and

(b) is a monomer of one of the following formulas:

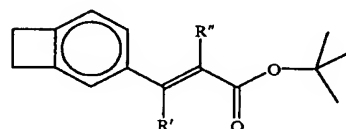


(i)



(ii)

and



(iii)

wherein

R' and R'' are independently selected from hydrogen, alkyl groups of 1 to 6 carbon atoms, aryl groups, or R' and R'' taken together from a cyclic group of 4 to 8 carbon atoms;

Z is a carbon-to-carbon bond or an aryl group;

x is an integer from 0 to 3;

y is 0 or 1; and

Z² is an aryl group.

* * * * *